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STARK EFFECTS ON THE LOWEST $^1B_{1g}(n\pi^*)$ STATE OF *p*-BENZOQUINONE

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Stark effects on the optical absorption spectrum of the lowest singlet state in *p*-benzoquinone (PBQ)-h_4 and -d_4 single crystals at 1.8°K are reported. The singlet origin components in PBQ-h_4 at 20057.8 cm^{-1} and 20061.3 cm^{-1} are shown to be states of opposite parity. The Stark experiments yield a transition moment between these levels of 2.2. ±0.1D ($E_b = 1.6E_{eff}$) for both PBQ-h_4 and -d_4.

Polarization experiments on the lower energy origin expose its magnetic dipole character and this state is assigned as a state of B_{1g}-total symmetry. A sizeable deuteration effect on the oscillator strength of this B_{1g} origin is also reported and discussed. Vibronic lines up to 1000 cm^{-1} from the origin lines also have been studied in external electric fields and these results are reported as well. A qualitative discussion of these results is given on the basis of a double minimum potential model for the lower $^1B_{1g}(n\pi^*)$ state. Arguments pro and contra this model are presented and the alternative of two close lying $^1B_{1g}(n\pi^*)$ and $^1A_u(n\pi^*)$ states is explored as well.

1. Introduction

p-Benzoquinone (PBQ)[$L=z(B_{1u}), M=y(B_{2u})$] as a prototype aromatic diketone, is expected to show numerous excited states in a narrow energy span. Recent ab initio SCF calculations [1] on the ground and lower excited states show that in the energy range of 4.21 to 4.67 eV five different electronic states are to be expected, viz., $^3B_{1g}(n\pi^*)$, $^3B_{3g}(\pi\pi^*)$, $^3A_u(n\pi^*)$, $^1B_{1g}(n\pi^*)$ and $^1A_u(n\pi^*)$. Most surprisingly though is the fact that the lowest triplet level is calculated to be $^3B_{1u}(\pi\pi^*)$ at 2.49 eV. The corresponding electric dipole allowed singlet state $^1B_{1u}(\pi\pi^*)$ is calculated at 7.12 eV.

Obviously these results do not agree very well with experimentally observed excitation energies on an absolute scale, e.g., singlet $B_{1u}(\pi\pi^*)$ is observed [2] at 5.12 eV, but the level ordening seems quite indicative and especially the calculated congestion of ($n\pi^*$ type) electronic states in a narrow energy range is in agreement with absorption experiments that have been done [2, 3]. Most of the disagreement on an absolute scale is possibly due to neglect of configuration interaction in these calculations and thus to a neglect of the difference in correlation energy among the different states. For similar type excitations one expects these correlation energies to be of similar magnitude and the calculated splittings of the $B_{1g}(n\pi^*)$ and $A_u(n\pi^*)$ triplet and singlet states as 662 and 1017 cm^{-1} possibly survive CI refinements. Anyway the best one can do at the moment is to compare these numbers with the claimed observed splittings of 225 and 320 cm^{-1} of these states in pure PBQ-h_4 [2]. From a detailed study of the gasphase spectrum of PBQ-h_4 and -d_4, Hollas et al. [3] made a fairly complete analysis of the rotational structure of a number of bands appearing in the lowest observed triplet and singlet state regions, using symmetric top band contour analysis. It was concluded that the lowest triplet state in the gasphase is $^3A_u(n\pi^*)$ at 18682 cm^{-1} with the lowest singlet state being $^1B_{1g}(n\pi^*)$ at 20030 cm^{-1}, with most of the intensity in the B_{1g}-state being vibronically induced by a_u and b_{3u} vibrations. No definite indications for the presence of the $^3B_{1g}(n\pi^*)$ or $^1A_u(n\pi^*)$ states were found, however. Trommsdorff [2, 4] has presented a very detailed analysis of the polarized single crystal spectra of PBQ and its methyl derivatives and concluded that in PBQ the lowest triplet and singlet state are of $B_{1g}(n\pi^*)$ symmetry, with the corresponding $A_u(n\pi^*)$ states 320 and 255 cm^{-1} to higher energy. The assigment of the lowest triplet state in the PBQ crystal at 18620 cm^{-1}

as $^3B_{1g}(n\pi^*)$ is, however, not in agreement with the quoted ab initio SCF calculations [1] which place triplet $B_{1u}(\pi\pi^*)$ as the lowest triplet state. This (calculated) result is in agreement with an earlier analysis of the PBQ-h_4 and -d_4 spectrum by Klump and McClure [5, 6] who assigned the triplet state at 18620 cm^{-1} as the benzenelike lowest triplet state $^3B_{1u}$ $(\pi\pi^*)$. We became interested in this problem and decided to perform Stark effect measurements on the lower excited states of PBQ to obtain a better insight in their electronic nature. A definite proof for the nearbyness of B_{1g} and A_u $n\pi^*$ states would be the observation of electric field induced repulsion between these sets of states. In a previous paper [7] we have shown that high resolution second order Stark effect measurements at low temperatures are quite feasible and that large effects are to be expected in molecules with nearby states of opposite parity. PBQ retains its molecular inversion symmetry in the crystal [8] and thus only second order Stark effects on its absorption spectrum are to be expected. The Stark effect matrix element that connects $A_u(n\pi^*)$ and $B_{1g}(n\pi^*)$ states is $\langle A_u|ez|B_{1g}\rangle E$ and the transition moment $\langle A_u|ez|B_{1g}\rangle$ has already been calculated by Edamura and Kanda [9] to be 22.0 D.

One can easily calculate that with a transition moment of this size and gaps between A_u and B_{1g} $n\pi^*$ states of a few hundred wavenumbers large second order electric field effects are to be expected at easily obtainable electric fields (~ 60 kV/cm). We have performed a detailed Stark effect study on pure and mixed-crystals of PBQ-h_4 and -d_4 between 18600 and 21000 cm^{-1}. Large electric field effects were observed in the triplet state regions and drastic effects in the lowest singlet state region. We have also carefully studied the optical absorption spectrum of proto-deutero mixed crystals of PBQ and obtained some relevant information on bandstructure properties of the lower excited states. We hope to communicate these results in a later paper. In this paper we only wish to report results of our Stark effect measurements on pure PBQ-h_4 and -d_4 crystals in the lowest singlet state region†.

† During the final Stark experiments on pure PBQ-h_4 and -d_4 crystals in the singlet state region we noticed that Johnson and Trommsdorff [10] also performed Stark modulation experiments on PBQ-h_4. Their results (although less detailed) essentially agree with ours on the absorptions studied.

In a following paper we hope to report results obtained from Stark modulation experiments on the lower triplet states.

2. Experimental

The crystal structure of PBQ is such [8] that in- and out of plane polarization and electric field effects can be easily separated. All the long molecular axes lie in the $(20\bar{1})$ cleavage plane, with the molecular planes tilted only 3° from it. The unit cell contains two molecules in a monoclinic packing ($P_{2_1/a}$) and molecular inversion symmetry is retained at the site.

All electric field effects reported here, were obtained with the electric field parallel to the crystal b axis. Similar effects were observed for the electric field parallel to the $p(102)$ axis and virtual no effects were observed for electric fields perpendicular to the cleavage (almost molecular) plane.

The PBQ crystals were grown in Bridgeman style from recrystallized and over CrO_3 sublimed material. Thin slices of the crystals grown were cut using a chemical saw and only those that after this operation still extinguished perfectly under the polarizing microscope were used in the polarized Stark absorption experiments reported here. The Stark effect measurements were performed in a manner as described previously [7] with one important change, that now the recorded Stark effect signal was the result of the ac-detected signal divided by the dc-detected signal. The signal obtained in this manner thus represents directly a percentage change in absorption versus wavelength. A $\frac{3}{4}$ meter 1702 SPEX was used at the second order of a grating with blaze at 1μ as the dispersing element in our Stark set up. All experiments reported here were performed at ~ 1.8°K.

3. Results

The lowest singlet absorption spectrum of PBQ-h_4 in the pure crystal has been reported previously [4, 5] and most of its intensity is vibronically induced. Its assignment as singlet $B_{1g}(n\pi^*)$ seems unquestionable [2] and its electronic origin at 20060 cm^{-1} in the pure crystal is only 30 cm^{-1} blue shifted with respect to the gasphase [3]. The electronic origin in the crystal is a doublet with a splitting of 3.5 and 2.8 cm^{-1}

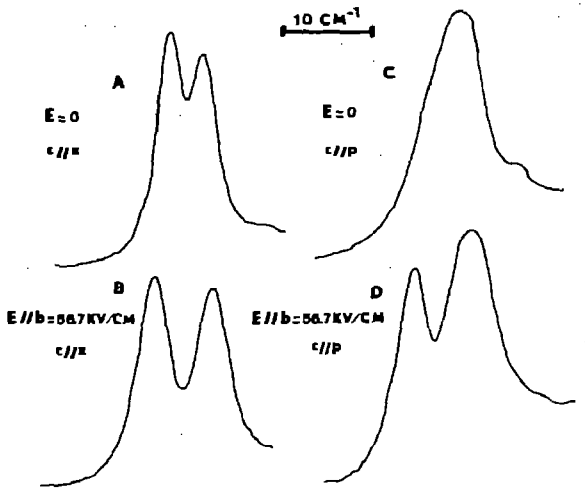

Fig. 1. The polarized absorption spectrum at 20060 cm^{-1} of the lowest singlet state origin in PBQ-h_4. In figs. 1a and 1b the E vector of the electromagnetic radiation (ϵ) is out of plane ($\epsilon // x$) polarized, while 1c and 1d show the inplane polarized spectra ($\epsilon // p(102)$ axis). Figs. 1b and 1d show the effect of an electric field (E) parallel to the crystal b axis.

for PBQ-h_4 and -d_4, respectively. This splitting has been explained previously as being due to factor group splitting of the B_{1g} origin in the crystal [11].

Fig. 1 shows this singlet origin of PBQ-h_4 in polarized light. The lower energy component at 20057.8 cm^{-1} only appears with the electric vector perpendicular to the molecular plane. Polarization experiments on the $(20\bar{1})$ cleavage plane show that the lower energy line is weakest with the electric vector parallel to the crystal b axis. We therefore conclude that this line is a *magnetic* dipole allowed transition and represents a state of $B_{1g}(R_z)$ total symmetry. The higher energy component is mainly electric dipole (in plane) allowed. The intensity imbalance among the origin doublet components is drastically changed on going from PBQ-h_4 to PBQ-d_4. In PBQ-h_4 the lower energy component (g) is more intense than the higher energy (u) component under conditions as specified in fig. 1. In PBQ-d_4 the opposite situation occurs. This can be seen in fig. 2, where the p-polarized origins at the $(20\bar{1})$ cleavage plane are shown. For PBQ-d_4 there is only a slight indication of the existence of a lower energy component. Fig. 1 also shows the effect of an in-plane (parallel to the crystal b axis) electric field on the origin components of PBQ-h_4. In an electric field the states repel one another and this shows that both components have *different parity* under inversion. The higher energy doublet component thus has u character and in an electric field the doublet components acquire mixed polarization characteristics. The dou-

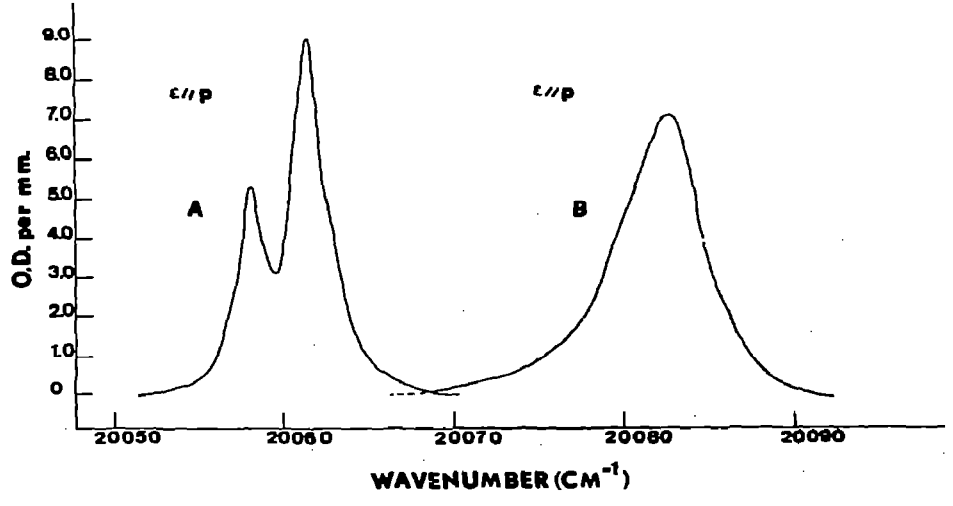

Fig. 2. Optical densities per mm of the p-polarized origins of PBQ-h_4 and -d_4 with the incoming light perpendicular to the $(20\bar{1})$ cleavage plane. The doublet at 20060 cm^{-1} (A) is due to PBQ-h_4 and the single line at 20080 cm^{-1} (B) represents the PBQ-d_4 origin absorption.

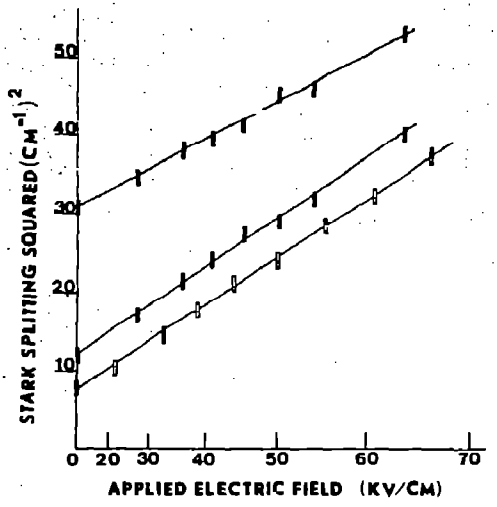

Fig. 3. Stark splittings of the origin lines at 20060 cm^{-1} in PBQ-h_4 and 20080 cm^{-1} in PBQ-d_4 are shown as a function of an external electric field parallel to the crystal b axis. The solid rectangulars refer to PBQ-h_4 and the open ones to PBQ-d_4 splittings. The upper curve shows the splitting of a vibronic line at 20867 cm^{-1} in PBQ-h_4.

ble[4] splitting squared as a function of external electric field is shown in fig. 3 for the origins of both PBQ-h_4 and -d_4. The experimental points are fitted to the following relation

$$\Delta^2 = \epsilon^2 + 4\langle g|er|u\rangle^2 E^2 ,$$

where Δ is the doublet splitting ϵ the zerofield doublet splitting (ZFDS), $\langle g|er|u\rangle$ a transition moment and E the external electric field.

From the fact that the electric field splitting is smaller with the electric field parallel to the p(102) axis and no electric field effect is observed for E perpendicular to the molecular plane, we identify from now on r with z. One now calculates that

$$\mu_{gu} \equiv \langle g|ez|u\rangle = 2.2 \pm 0.1\text{D} \quad (E_b = 1.6\, E_{eff})$$

and fig. 1 shows that this number is virtually independent of deuteration. The u state is now identified as a state of A_u total symmetry. That this doubling of the origin is a true molecular phenomenon and not a crystal field effect (such as factor group splitting) can be seen from the electric field effect on a proto deutero mixed crystal of PBQ-d_4. Fig. 4 shows the electric field modulated absorption spectrum of a PBQ-d_4 crystal containing ~ 10% PBQ-d_3h and ~ 1% PBQ-dh_3. All the isotopic impurity lines split in an electric field and this is definite proof for the molecular origin of the effects observed. We have also studied the Stark effect of all sharp vibrations occurring in the singlet absorption spectrum up to 1000 cm^{-1} from the origin in both PBQ-h_4 and -d_4. Most of the

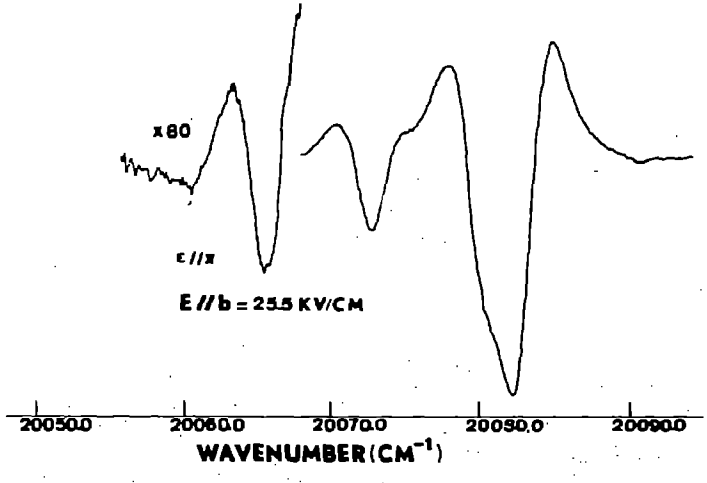

Fig. 4. The Stark modulated absorption spectrum of the singlet origin in a PBQ-d_4 crystal containing 10% PBQ-d_3h and 1% PBQ-dh_3 is shown. The ac electric field of 51 kV/cm (top–top) is parallel to the crystal b axis.

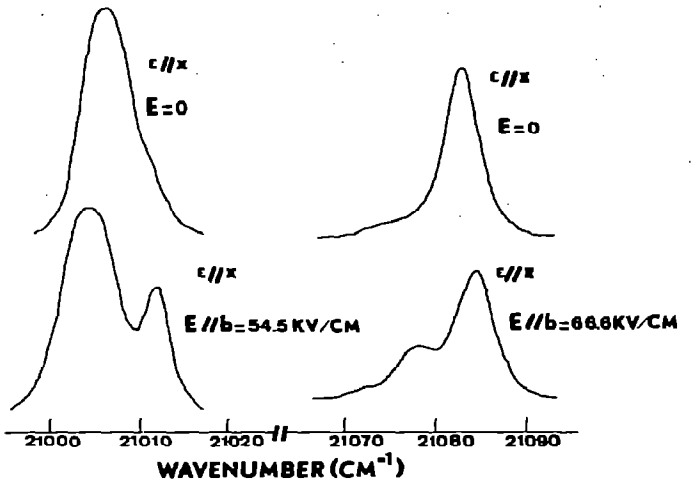

Fig. 5 Effect of an electric field (parallel b) on some vibronic lines in the singlet absorption spectrum. The line at 21006 cm^{-1} is a PBQ-h_4 and the one at 21086 cm^{-1} a PBQ-d_4 absorption.

Table 1
Splittings and transition moments of vibronic lines in the lowest singlet excited state of PBQ-h_4 and -d_4

Line position[1] (cm^{-1})		Splitting[2] (cm^{-1})	Transition moment[3] (D)
20057.8	(origin)	3.5 ± 0.1	2.2 ± 0.1
20061.3	(origin)		
20765	(b_{1u})	5.6 ± 0.2	1.8 ± 0.2
20867	(a_g)	5.6 ± 0.1	1.9 ± 0.1
20893	(b_{3u})	9.0 ± 0.4	1.3 ± 0.3
21006	(a_u)	5.9 ± 0.2	1.9 ± 0.2
20079.9	(origin)	2.7 ± 0.1	2.2 ± 0.1
20082.6	(origin)		
20433	(a_u)	5.1 ± 0.2	1.9 ± 0.2
20805	(a_g?)	5.4 ± 0.2	1.9 ± 0.2
20840	(a_u)	4.6 ± 0.2	2.2 ± 0.2
21086	($b_{?g}$)	4.6 ± 0.2	1.9 ± 0.2

1) The line positions are given in vacuum wavenumbers and symmetry labels are adopted from refs. [2] and [3].
2) The splittings have been derived from extrapolation to zero electric field.
3) These transition moments are calculated with the assumption $E_b = 1.6\,E_{eff}$. The relative magnitude of the transition moments are accurate at least to within 5%.

vibrations appear as single lines, but in an electric field, lines are induced at higher energy. An example is shown in fig. 5. In PBQ-d_4 we have found one vibration where a lower energy component is induced in an electric field and this is also shown in fig. 5. From the observed electric field splittings of the vibronic lines one is able to find the ZFDS and vibronic transition moments and these numbers are given for some selected vibrations in table 1. The vibronic transition moments are calculated from curves as given in fig. 3 and the electric field splittings of one of the PBQ-h_4 vibronic lines (appearing at 20867 cm^{-1}) is also given in this figure. This particular vibronic component in zero electric field already shows up as a doublet with a ZFDS of 5.3 cm^{-1}. The intensity distribution among these components is very similar to the origin doublet components for the electric vector of the radiation out of plane polarized, but the lower energy component is still present for in-plane polarized radiation, unlike the lower energy component of the origin doublet.

The transition moment of this vibronic doublet is calculated to be 1.9 ± 0.1D ($E_b = 1.6\,E_{eff}$) and as it is measured on the same crystal as the origin transition moment, is clearly smaller. From table 1 one can see that practically all vibronic transition moments are smaller than the pure electronic ones.

4. Discussion

The first intriguing question to be settled in a discussion about the Stark effects presented here is: do the origin components of the lowest singlet excitation belong to the same electronic [$^1B_{1g}(n\pi^*)$] state or do they represent origins of *different* electronic [$^1B_{1g}(n\pi^*)$ and $^1A_u(n\pi^*)$] states. The observed decrease in intensity of the lower energy component of this origin doublet on deuteration, we feel, is a strong argument in favour of assigning these levels as *vibrational* levels of one electronic [$B_{1g}(n\pi^*)$] state. The splitting of the $^1B_{1g}(n\pi^*)$ origin must then be due to inversion doubling. This interpretation has also been suggested by Johnson and Trommsdorff in their announcement of the Stark effect on this state. Close lying electronic states of different symmetry are expected to perturb one another very strongly. In PBQ, the $^1B_{1g}(n\pi^*)$ and $^1A_u(n\pi^*)$ states are possibly split only by a few hundred wavenumbers and in such a situation the lower electronic state may acquire a double minimum potential along one or more of the vibronically perturbing b_{1u} normal modes [12].

In the PBQ pure crystal, all u type modes are mixed through the crystal field and all u type vibrations are thus expected to participate in this vibronic coupling. This means that the excitation of any u type mode may change the inversion level spacing and thereby its electric field effect, as is being observed. Also the decrease, on deuteration of the inversion doubling is consistent with the double minimum potential model. As yet, we have not been able to locate in the spectrum, inversion levels belonging to excitations of the promoting b_{1u} mode. The only b_{1u} mode observed (ν_{16}) behaves quite similar to the other u type modes in the spectrum (see table 1).

The site symmetry in the PBQ crystal is such [8] that the lower energy B_{1g} origin (g inversion level) is expected to remain purely magnetic dipole allowed, as is observed. The appearance of the u inversion level (A_u total symmetry) can be understood, when we consider it to be a false origin. While in the gas-phase this level must be strictly forbidden, in the crystal the crystal field allows u type (electric dipole) intensity to be induced in this state. Polarization measurements on the $(20\bar{1})$ cleavage plane, show the $^1B_{1u}(\pi\pi^*)$ state to be predominant in this mixing. Assuming now the double minimum potential to be adequately described by a sum of two symmetrically displaced harmonic oscillators, than the measured transition moments can be explained as *dipole moments* of the PBQ molecule in distorted configurations. The magnitude of the distortion depends on the particular vibronic level involved, but is independent of deuteration as is observed. The inversion splittings being determined by the gap between the levels in the well and the barrier top, decrease on deuteration as expected. The minimum energy configuration in the lowest $^1B_{1g}$ ($n\pi^*$) singlet state of PBQ is thus reached by an asymmetric configuration of the oxygen atoms with respect to the ringsystem. As most of the excitation density in this transition is on the oxygen atoms, we expect the $b_{1u}(\nu_{13})$ C=O stretching mode to be dominant in the vibronic coupling between the $^1B_{1g}(n\pi^*)$ and $^1A_u(n\pi^*)$ excitations. Most of the results presented here can also be explained on the basis of nearly degenerate $^1B_{1g}(n\pi^*)$ and $^1A_u(n\pi^*)$ states. The origin polarizations are easily understood; the u component is crystal field induced, while the g component is intrinsically magnetic dipole allowed. The variation in ZFDS is simply related to anharmonicity of the various modes, while the vibronic transition moments are the electronic ones multiplied by Franck–Condon factors. We consider the latter explanation very unlikely, as it, e.g., fails to explain the vibronically induced part of the absorption spectrum. We therefore believe that the double minimum potential model for the lowest $^1B_{1g}(n\pi^*)$ state in PBQ is essentially correct. More detailed calculations on the basis of this model for the excited state structures of the lowest triplet and singlet $B_{1g}(n\pi^*)$ states will be presented in a following paper.

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References

[1] H.T. Jonkman and W.C. Nieuwpoort, to be published.
[2] H.P. Trommsdorff, J. Chem. Phys. 56 (1972) 5358.
[3] J.M. Hollas, Spectrochim. Acta 20 (1964) 1563; J. Christoffersen and J.M. Hollas, Mol. Phys. 17 (1969) 655.
[4] H.P. Trommsdorff, Chem. Phys. Letters 10 (1971) 176.
[5] K.N. Klump, Ph.D. Thesis, University of Chicago, USA (1968)
[6] D.S. McClure, Excitons, magnons and phonons in mol. crystals (Cambridge Univ. Press, Cambridge, 1968) p.165.
[7] J.H. Meyling and D.A. Wiersma, Chem. Phys. Letters 20 (1973) 383.
[8] J. Trotter, Acta Cryst. 13 (1960) 86.
[9] T. Edamura and Y. Kanda, Mem.Fac.Sci. Kyusku Univ. Ser. C 6(2)-71-3(1968).
[10] L.W. Johnson and H.P. Trommsdorff, Proc. 6th Mol. Cryst. Symp., Elmau, Germany (1973) p.86.
[11] H.P. Trommsdorff, J. Kahane-Paillons, Compt. Rend. Acad. Sci. (Paris) 270B (1970) 960.
[12] R.M. Hochstrasser and C.A. Marzzacco, in: Molecular luminescence, ed. E.C. Lim, (Benjamin, New York, 1969) p.631.